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**RECOVERY OF STYRENE MONOMER VAPOR FROM ACTIVATED  
CHARCOAL WITH AND WITHOUT METHYL ETHYL KETONE PEROXIDE  
ACTIVATION**

**BY**

**ALAN ELI JESSEN**

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A Thesis Submitted to the Faculty of the  
**DEPARTMENT OF PHARMACOLOGY AND TOXICOLOGY**

In Partial Fulfillment of the Requirements  
For the degree of

**MASTER OF SCIENCE  
WITH A MAJOR IN TOXICOLOGY**

In the Graduate College  
**THE UNIVERSITY OF ARIZONA**

1996

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This thesis has been approved on the date shown below:

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Assistant Professor  
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## ABSTRACT

A laboratory study was conducted to evaluate the stability of styrene monomer (SM) with and without the presence of an initiator on 100mg/50mg activated coconut charcoal tubes in accordance with NIOSH Method 1501, Hydrocarbons, Aromatic. The stability of SM was tested over time (0, 1, 3, 7, and 14 days), with various styrene vapor loadings (1, 2, 5, 8, and 10 ul). In addition, five ul of styrene monomer was vaporized in the presence of an initiator and deposited on charcoal tubes. These tubes were then analyzed after storage times of zero, one half, one, two, four, twenty-four and forty-eight hours. Styrene vapors, deposited on the activated carbon matrix with and without the presence of the initiator methyl ethyl ketone peroxide, were completely recovered. Polymerization, either self induced or initiated by methyl ethyl ketone peroxide, was not a factor in this recovery.

## I. INTRODUCTION

It is important for health and safety professionals not to assume that air sampling always provides accurate estimates of exposures. Methods need to be challenged against one another and validated under controlled conditions against factors which may confound measured estimates of the level of airborne pollutants in the field.

This investigation was initiated following suspected inconsistencies in air sampling for styrene monomer (SM) in a synthetic marble production facility. Charcoal tube results appeared inconsistent with indicator tube and infra red (IR) analyzer measurements collected over similar time frames. At this facility for example, charcoal tubes indicated a time weighted average (TWA) over a 165 minute period of 57 ppm of styrene. Yet the TWA, estimated over this same period of time by IR analysis and substantiated by indicator tubes, was between 100 and 125 ppm of styrene. Although the indicator tubes and IR analysis reflect averaged, repeated, instantaneous measurements of SM to calculate the TWA rather than a continuous collection system like charcoal tubes, the estimated differences in the TWA are too great to ignore. These discrepancies were noted during multiple assessments of the manufacturer's environment. The possibility of a discrepancy lead to a review of NIOSH Method 1501, Hydrocarbons, Aromatic used in

the measurement of styrene in occupational environments. It was suspected that SM may self polymerize and/or adhering to the activated charcoal beds leading to lower estimates of measured SM. Additionally, SM may be mixed and sprayed during industrial processes with the initiator (accelerator), methyl ethyl ketone peroxide (MEKP). It was suspected that SM losses may be due to this chemically induced polymerization of SM deposited on the activated charcoal tubes.

Unlike other chemical agents determined using NIOSH Method 1501, Hydrocarbons, Aromatic (NIOSH Manual of Analytical Methods (NMAM), fourth edition, 8/15/94), SM is a self polymerizer (See Figure 1). This chain reaction may also be facilitated or accelerated by the presence of the free radical initiator MEKP, as is found in industrial applications. Styrene polymerized by either of these mechanisms may therefore be unavailable for analysis using NIOSH Method 1501. The degree of polymerization, self or initiated, may be dependent on time and/or concentration.

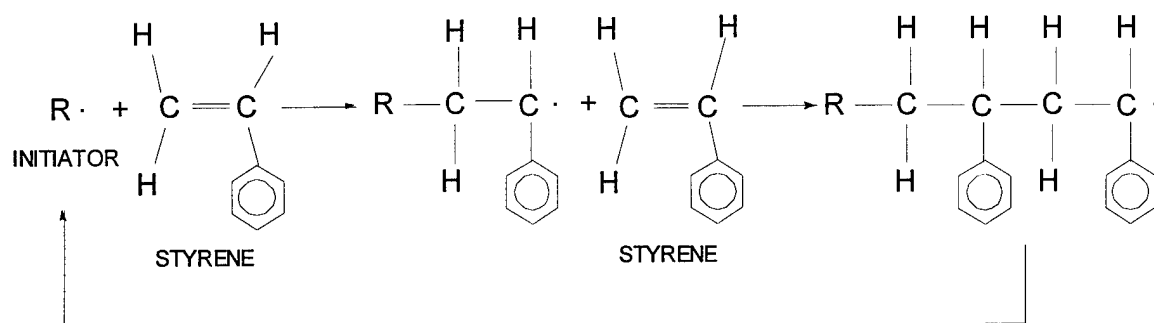


Figure 1: Styrene Polymerization Reaction

## II. LITERATURE REVIEW

### Styrene Monomer Uses

In 1989 the U.S. produced over 9 billion pounds of SM. Over 300,000 Americans are exposed to the SM in pure or mixed forms on a daily basis (ACGIH, 1991). SM is used in a multitude of "plastic" products including wire insulators, Styrofoam<sup>®</sup>, fiberglass, adhesives, synthetic marble, molded plastics, rubber tires and beads. The majority of the molded or shaped plastics found today are SM products.

The properties of the end product, such as strength, rigidity, chemical and heat resistance, are adjusted by limiting the average length of the polymer or the type or amount of additives. These modifications are accomplished by adjusting the curing temperature and the additives used such as rubber co-polymers (styrene-butadiene), vinyl ketone (allows for degradation in sunlight), fire retardants, or various other co-polymers such as acrylonitrile (Brighton 1979).

## **Toxicology**

### **General (Human)**

The main target organs of styrene are the liver and the nervous system. However, the renal system is regarded as the earliest, detectable effect for styrene on an organ. The effect starts above a 22 ppm exposure over eight hours according to NIOSH (DHHS 1992). Above this level, quantities of the metabolites mandelic acid and phenyl glyoxylic acid in the urine are above normal levels for the individual. This designated no observable effect level (NOEL) of 22 ppm, is the point above which the liver metabolites are expected to be elevated in humans. Though the NOEL is designated as a renal effect, it reflects more on the liver, which produces these substances, than a direct effect of styrene on the kidney. Toxic liver effects of SM occur at prolonged exposures to 100 ppm and take the form of an elevation in serum amino transferase (DHHS, 1994).

Central nervous system (CNS) depression has been detected in humans exposed to SM between 55 and 99 ppm based on several CNS function tests (DHHS 1992). However, statistical increases in EEG abnormalities have been detected with chronic exposure to as low as 31 ppm in humans (Cherry, 1991). A more recent study has shown that chronic

exposure to as low as 25 ppm SM caused significantly lower scoring on the Farnsworth 100 Color Hue test (Fallas, 1992). Workers exposed to SM in this study had problems in red-green and blue-yellow visual acuity. This was a stratified case control study of 120 workers.

### **Acute Toxicity (Humans)**

The common symptoms associated with acute SM exposure in humans are related to irritation and mild CNS depression. These symptoms include conjunctivitis, nasal irritation, nausea, drowsiness, lightheadedness, ataxia, and memory loss (ACGIH, 1991). Like other organic solvents, styrene is also a defatting agent. Skin exposed to styrene becomes dry and brittle, leading to a form of dermatitis.

A thirty minute inhalation of 350 ppm styrene results in a decrease in ocular tracking ability. Eye and respiratory irritation begin at 200 ppm (DHHS, 1992). CNS depression is significant at 200 ppm over 4 hours (WHO, 1983).



Higher exposures in humans result in continued respiratory depression with CNS "intoxication". Death results from a combination of loss of consciousness, respiratory depression, respiratory tract inflammation, and oxygen displacement (WHO, 1983). The immediately dangerous to life or health (IDLH) point for styrene is 700 ppm (DHHS, 1994), recently decreased from 5,000 ppm.

Liver and kidney damage related to SM is minimal since death from the CNS effects occur before significant toxicity to these organs. Increases in liver enzymes following short exposures above 300 ppm do occur (DHHS, 1992).

### **Chronic Toxicity (Humans)**

Chronic exposure to 50 to 100 ppm styrene causes an increase in complaints of headache, dizziness, and nausea. A decreased reaction time, a feeling of weakness, and a 2-8% reduction in workers' peripheral nerve conduction velocities (ACGIH, 1991) have been noted. Chromosomal aberrations among styrene workers have not been consistently found. Some small studies have shown chromosomal damage but lacked statistical significance. Other larger studies did not show damage (ACGIH, 1991; DHHS, 1992; WHO, 1983). Liver enzymes are elevated at exposures over 100 ppm (DHHS, 1992). At

this level, the elevation of liver enzymes are statistically significant but not biologically meaningful in that the functioning of the liver seems unaltered.

To date, human chronic exposure studies have not shown an increase in reproductive problems, cancers, or hematopoietic disorders (ACGIH, 1991; DHHS, 1992). Studies that have suggested problems were not statistically large or were reproducible (ACGIH, 1991). One problem with many of the human SM exposure studies is that they relied on extrapolated exposure measurements. Another problem with these studies in the industrial setting is that the additives employed as co-polymers and initiators were more toxic than the SM. The presence of these toxic chemicals confounds many industrial epidemiological studies addressing the health effects of styrene.

### **Animal Studies**

Most animal studies with SM have been performed on rats and mice. Maternal toxicity is encountered before reproductive or fetal toxicity can be detected. Animal studies have not shown increases in cancer rates beyond those noted in historical controls.

Studies of SM chromosomal damage are ambiguous. While chromosomal damage (abnormalities) studies detected in rats inhaling 300 ppm of SM, 6 hours/day for 2-3 months and in mice given a single I.P. dose of 250-1000 mg/kg SM, chromosomal damage was not shown in rats inhaling 600 to 1000 ppm of SM, 6 hours/day for 12 months (ACGIH, 1991; WHO, 1983).

Mice are the most sensitive species to SM toxicity. One study reported significant deaths in male and female mice after exposure to as little as 500-600 ppm for three 8 hour daily exposures due to liver failure (Morgan, 1993a). Unique to mice is that the B6C3F1 strain of male mice, which is often used in cancer studies, appears to be very sensitive to SM toxicity (Morgan, 1993b), although this is not consistently found with other strains of mice, male or female (Morgan, 1993c). The only study linking cancer to SM was a chronic exposure rat and mouse study showing an increase in pulmonary adenomas in only the male mice (B6C3F1). This level of cancer (pulmonary adenomas and carcinomas), incidentally, was within the historical levels of controls (ACGIH, 1991).

Rats, unlike mice, do not die of liver damage. They, like humans, succumb to the CNS depressant effects. Glutathione depletion in the liver and kidneys plus an increase in liver enzymes occur with an exposure of 300 ppm for thirty hours spread over a five day period (WHO, 1983). However, rats exposed to 1300 ppm for forty hours a week for six

months had no deaths associated with styrene exposure (ACGIH, 1991). An exposure of 10,000 ppm for four hours caused mucous membrane and eye irritation and CNS depression with marked pulmonary lesions (Brighton, 1979).

### **Toxicology Summary**

Chronic styrene exposure studies in humans, mice, and rats do not show reproductive, teratogenic, hematopoietic, or renal toxicity. There are significant differences in the kinetics of styrene metabolism between species which probably explains the differences in sensitivity to SM.

The EPA has labeled SM as a possible carcinogen in humans on the basis of the following information. The Ames test is positive. There were a few limited studies with SM exposed industrial workers suggesting chromosomal damage. There were several positive animal chromosomal damage studies. And finally, there was the one mouse study showing a possible carcinogenic effect on the lungs (B6C3F1 male mice) previously mentioned (ACGIH, 1991; DHHS, 1992; WHO, 1983). In most of these industrial worker studies showing increased chromosomal damage, however, the workers were not exposed to pure SM. Chromosomal damage was not found in larger similar

studies (Anderssen, 1980; Norppa, 1991).

Based on this information, the Environmental Protection Agency (EPA) has set the RfD (oral) dose (the dose at which a lifetime exposure would not be expected to have any adverse health effects) for SM at 0.2 mg/kg/day (DHHS, 1992). This assumes an oral intake and complete absorption of the styrene. To put things into perspective, a 70 kg worker would attain this level of styrene breathing 0.5 ppm SM, at a rate of three times normal resting tidal volume, over a 40 hour work week (assumes 67% of SM breathed is absorbed (DHHS, 1992)).

The EPA has also classified SM as a B2/C carcinogen (probable to possible carcinogen) with a cancer slope factor ( $q_1$ ) of 0.03 (mg/kg/day)<sup>-1</sup> (DHHS, 1992). The EPA believes that the previously mentioned 70 kg worker exposed to 1.12 ppm SM over a 40 hour work week over a life time would raise his risk of developing cancer by 1 in a million. However, this  $q_1$  is based on the increase in pulmonary adenomas in male mice from the one mouse/rat chronic exposure cancer study mentioned earlier (ACGIH, 1991). These EPA parameters (RfD and  $q_1$ ) are derived statistically by extrapolation of data.

Regardless of these derived parameters, there is clear evidence of toxic effects of SM on humans. Studies thus far have shown visual acuity changes at about 25 ppm, EEG

abnormalities at about 31 ppm chronic exposure and a CNS depressant effect at between 50 to 100 ppm chronic exposure (ACGIH, 1991). Around 25 to 50 ppm would seem to be the first point of noticeable reversible physical response in workers.

### **Current Exposure Limits (ACGIH, 1991; DHHS, 1992; WHO, 1983)**

The current limits of exposure to styrene for workers are based on its CNS depressant effect and mucosal irritation. Specific exposure limits or recommendations are presented in Table 1 for the prevention of the aforementioned effects.

EXPOSURE LIMITS		
ORGANIZATION	EXPOSURE	AMOUNT
<b>EPA</b>	RfD*	0.2 mg/kg/day
(Environmental Protection Agency)	q1**	$0.3(\text{mg/kg/day})^{-1}$
<b>ACGIH</b>	TWA***	50 ppm
(Am. Conference of Gov. Industrial Hygienists)	STEL^	100 ppm
<b>NIOSH</b>	TWA	50 ppm
(Nat. Institute of Occupational Health and Safety)	STEL	100 ppm
	IDLH†	700 ppm
<b>OSHA</b>	TWA (PEL‡)	100 ppm
(Occupational Safety and Health Administration)	STEL	200 ppm
<b>GERMANY</b>	TWA	20 ppm
<b>SWEDEN</b>	TWA	20 ppm
<b>UNITED KINGDOM</b>	TWA	100 ppm

\* RfD, Lifetime dose felt to have no ill effects

\*\* q1, Slope of a line used to determine exposure point where cancer increases by 1/1,000,000

\*\*\* Time Weighted Average (TWA), the exposure level below which an exposure of five, eight hour work days per week, would not be expected to harm workers.

^ Short Term Exposure Limit (STEL), the exposure level not to be exceeded for more than 15 minutes, no more than four times in a day with one hour in between.

† IDLH, Immediately Dangerous to Life and Health

‡ PEL, Permissible Exposure Limit

Table 1: Exposure Limits of Various Governmental and Consensus Groups

## **Styrene Monomer Stability on Activated Charcoal**

Current literature does not address the stability of SM on charcoal tubes with or without the presence of an initiator. In its Method 1501, NIOSH states that, "Storage stability has not been assessed." As a result, the possibility of self-induced or initiated polymerization or other losses of SM over time has not been evaluated. If these losses occur, then measured SM levels in the workplace would be artificially low and human exposures higher. In addition, toxicology and field studies used to determine the effects of SM on humans, may have underestimated the level of SM exposure required to induce an effect in humans (assuming the charcoal tube method was employed). If losses occur with SM, then measurements of other compounds that may polymerize on collection media would require re-evaluation.

A previous study (Faas, 1996) demonstrated that losses on stored charcoal tubes exposed to both SM and the initiator MEKP did not occur between twenty-four hours and two weeks. The study, however, did not determine if losses occurred prior to the twenty-four hour storage/analysis period (Faas 1996).

The Occupational Safety and Health Administration (OSHA) in 1989 recommended the use of p-tert-butylcatechol coated charcoal tubes (100/50 mg sections, 20/40 mesh) for



collection of SM. With this tube, charcoal desorption is with toluene and analysis with gas chromatography (FID). This method was not tested in this investigation.

### **III. OBJECTIVES**

The purpose of this study was to determine if SM collected during environmental assessments (real world conditions) is lost on the activated charcoal tube prior to desorption and GC analysis. Specifically, the study was designed to investigate whether SM is lost via self or initiated polymerization on activated carbon prior to analysis.

## VII. MATERIALS AND METHODS

### Standard Methodology

All styrene analyses performed throughout this investigation, unless specifically mentioned, conformed to the gas chromatographic (GC) procedures recommended in NIOSH Method 1501. A Hewlett-Packard, model 5890 GC equipped with a flame ionization detector was employed for all analyses. In place of the three meter 10% OV-275 column recommended by NIOSH, a six foot 10% OV-101 column was used for analyte separation. Integration of the GC chromatograms was performed using the JCL6000 Chromatograph Data System with version 4.25 software. The GC injection volume was limited to 2 ul, instead of the recommended 5 ul, to avoid saturating the gas chromatograph detector. All injections were performed manually using a 10 ul syringe. Desorption was with one milliliter of carbon disulfide with a minimum desorption time of 30 minutes. Injection and detection temperatures were 225 °C and the column temperature was 100 °C with nitrogen as the carrier gas.

In conformance with NIOSH Method 1501, styrene vapors were collected with coconut shell charcoal tubes, 100mg/50mg (SKC Lot 120). Air flows through the tubes were

monitored with a Gilian soap bubble flow meter (Giliblator pn: D-800268) with a standard 20 cc - 6 LPM bubble generator. Potential interferences noted in NIOSH Method 1501 are alcohols, ketones, ether, and halogenated hydrocarbons.

### **Quality Control Standards and Investigations**

Primary standards were prepared over a range of 0.08 to 10 ul/ml of SM in carbon disulfide using styrene monomer manufactured by Fisher Scientific Co., lot 702122. In addition, five ul of SM were added to one ml of carbon disulfide and tested regularly to ensure GC reproducibility throughout the investigations.

To ensure that styrene deposition on glass played no part in the amount of SM recovered the glass tubes and glass wool plugs, the 10 ul SM exposed tubes from the experiments were washed in carbon disulfide for 30 minutes and then analyzed.

To determine if trapped or residual SM was recovered from styrene polymers, two simple tests were conducted. In the first test, 10 ul of MEKP mixture (50 wt. % MEKP, 50 % wt. dimethyl phthalate, manufactured by Aldrich Chemical Co. Inc., lot 02729HT) (see Table 2 and Figure 2) were mixed with 10 ul of SM on a glass cover slip. The mixture

was then allowed to polymerize for one hour, desorbed in carbon disulfide, and analyzed by GC.

### **Vapor Verses Liquid Deposition/Recovery**

A quality control study was designed to examine differences in the recovery of SM from charcoal tubes using liquid and vapor deposition techniques. Five different aliquots of SM (1, 2, 5, 8, and 10 ul) were vaporized onto charcoal tubes in triplicate for a total of fifteen prepared tubes. Duplicate sets of fifteen tubes had the styrene imparted onto the charcoal in the vaporized form by placing the liquid SM onto the glass just inside the charcoal tube opening and drawing 0.25 to 0.30 LPM air through the tube for one half hour. One set of fifteen tubes was stored for zero hours and one set of tubes was stored for twenty-four hours before GC analysis.

Two additional sets of fifteen tubes were prepared with liquid styrene imparted directly onto the front section of the charcoal tube. However, in accordance with the NIOSH method 1501 protocol, the back section of the charcoal was removed, and then liquid SM was injected directly onto the charcoal. The five different aliquots of SM placed on the charcoal were: 1ul, 2ul, 4ul, 6ul, and 8ul. The tubes were then capped and stored for

<u>Name/synonym</u>	<u>Empirical Formula</u>	<u>Molecular Wt.</u>	<u>Boiling Pt. °C</u>	<u>Vapor Pressure</u>		<u>Density</u>
				<u>@25°C mmHg</u>		<u>@20°C g/ml</u>
Styrene (Vinylbenzene)	$C_8 H_8$	104.15	145.2	6.1		0.906
Methyl Ethyl Ketone Peroxide (MEKP, 2 butanone peroxide)	$C_8 H_{16} O_4$	176.21	118	Not available		1.170
Dimethyl Phthalate	$C_{10} H_{10} O_4$	194.19	283.7	<0.01		1.194

Table 2: Properties of Chemicals Used

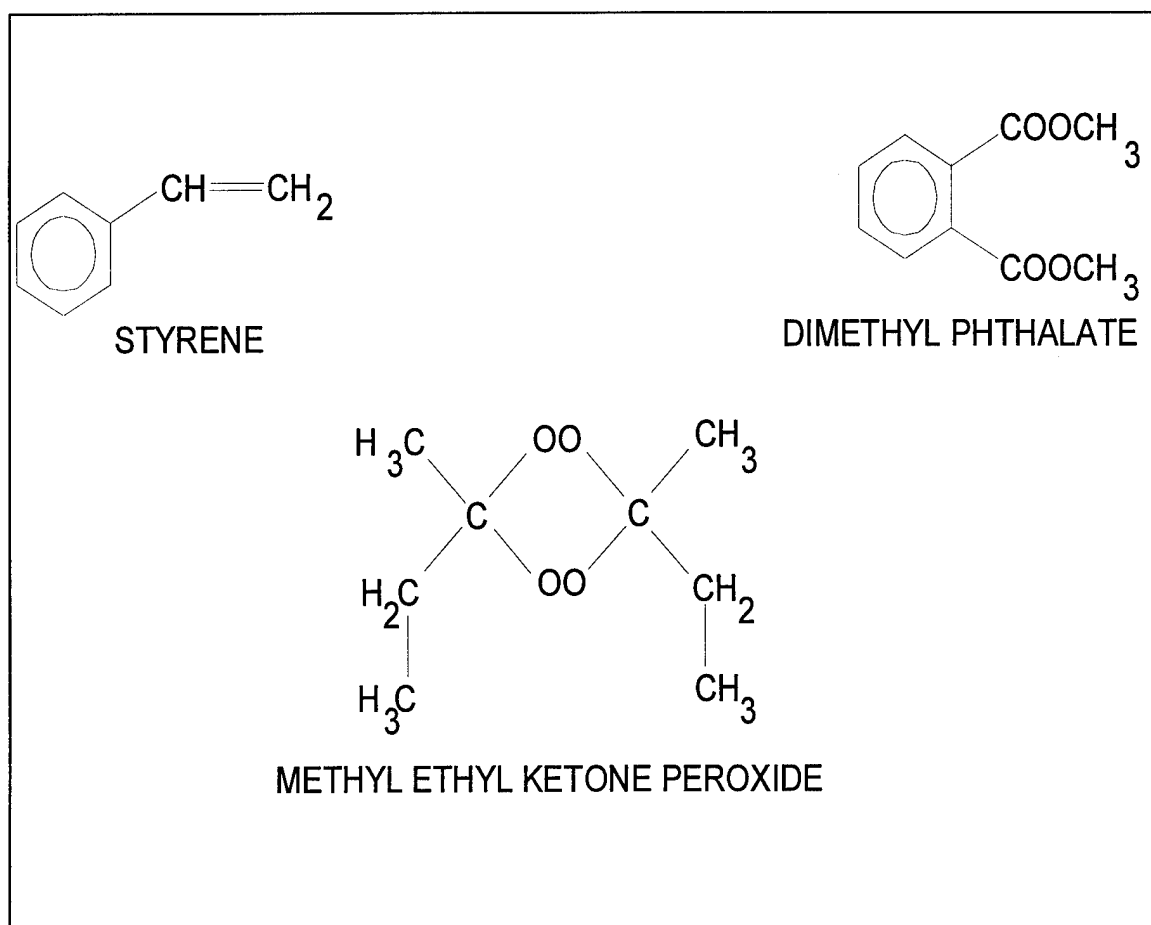


Figure 2: Structures of Chemicals Used

either zero or twenty-four hours before GC analysis, as described previously. The twenty-four hour storage period using liquid SM is the test condition recommended by NIOSH Method 1501 to determine desorption efficiency.

### **Recovery of SM Vapors From Charcoal Tubes**

A study to evaluate the recovery of SM from activated carbon was conducted under typical sampling conditions namely, room temperature, NIOSH recommended loading doses, and air flow rates suggested by NIOSH for monitoring SM. These are the guidelines most often used by industrial hygienists when air sampling SM in the field.

The recovery of vaporized SM from activated charcoal was tested over five storage periods. The storage periods were zero hours, twenty-four hours, seventy-two hours, one week, and two weeks. Triplicate tubes were prepared for each storage period at five different loadings of SM. These loadings were 1, 2, 5, 8, or 10 ul of SM for a total of fifteen tubes for each storage period tested. Charcoal tubes were attached to an air sampling pump with a flow rate adjusted to between 0.25 and 0.30 L/min. The liquid SM was then placed on the interior surface of the glass charcoal tube, just inside the inlet but prior to the glass wool plugs. The SM was vaporized and deposited onto the charcoal



tube over a one hour period. The tubes were then capped and stored at room temperature (between 20 and 26 °C) for subsequent analysis.

At the end of the storage period, tubes were analyzed by GC as previously described. Five GC injections were performed for each desorption; e.g. five injections from each desorption (i.e. front half or back half of each tube). The five injection averages were used to compute SM recovery at assigned loadings and storage times.

### **Recovery of Activated SM From Charcoal Tubes**

In evaluating the recovery of SM following vapor activation with MEKP, three different protocols were examined. The first two protocols served as controls. In the first, the charcoal tube was exposed to only SM vapors. In the second, the charcoal tube was exposed simultaneously to vapors of SM and to a component of the MEKP activator, dimethyl phthalate (DMP) (manufactured by Fisher Scientific Co., lot 773473). In the third, charcoal tubes were exposed to vaporized SM and the mixture of DMP and MEKP activator. (MEKP is unavailable in a pure form and the form used consisted of a 50% mix with DMP for stability, thus the DMP/SM test control.) In fact, the MEKP used in the previously mentioned synthetic marble facility represents a mixture of 34.3% MEKP

and 53% DMP (Trade name, Lupersol<sup>®</sup>, manufactured by ATOCHEM).

For each of the three test protocols, forty-two charcoal tubes were prepared (one loading, six replicates, and seven storage times). All sets were stored at room temperature before desorption and analysis. The storage times in this experiment were zero, one half, one, two, four, twenty-four, and forty-eight hours.

As shown in Figure 3, vaporized SM or vapor mixtures of SM and DMP or SM and DMP/MEKP were delivered to their respective charcoal tubes by placing aliquots of individual components onto separate ends of a glass Y to which were attached a 2 cm piece of glass tubing with glass wool plugs inside to enhance vaporization. The glass Y was connected to the inlet of an empty glass impinger mixing chamber. Air from the mixing chamber was collected on air activated charcoal tube using a sampling pump. All connections were made with a 1.5 to 2 cm length of tygon tubing (See Figure 3). Flow rates for each arm of the Y were adjusted to between 0.25 and 0.35 L/min.

After air flows were adjusted, chemicals were placed on the glass wool at each end of the two Y ends. In the first test condition, 5 ul of SM were placed on the glass wool in one end of the Y and nothing in the other end. In the second test condition, 5 ul of DMP were placed on one end of the Y and then 5 ul of SM were placed on the other end. For the

third test protocol, 5 ul of the MEKP/DMP mixture were placed at one end of the Y and then 5 ul of SM were placed on the other end.

The tubes were then removed, capped and stored for designated time periods at room temperature. The glass wool plug and its section of glass tubing were discarded after each run to prevent possible chemical carry-over. Tubes were then analyzed by GC. Each sample was injected five times.

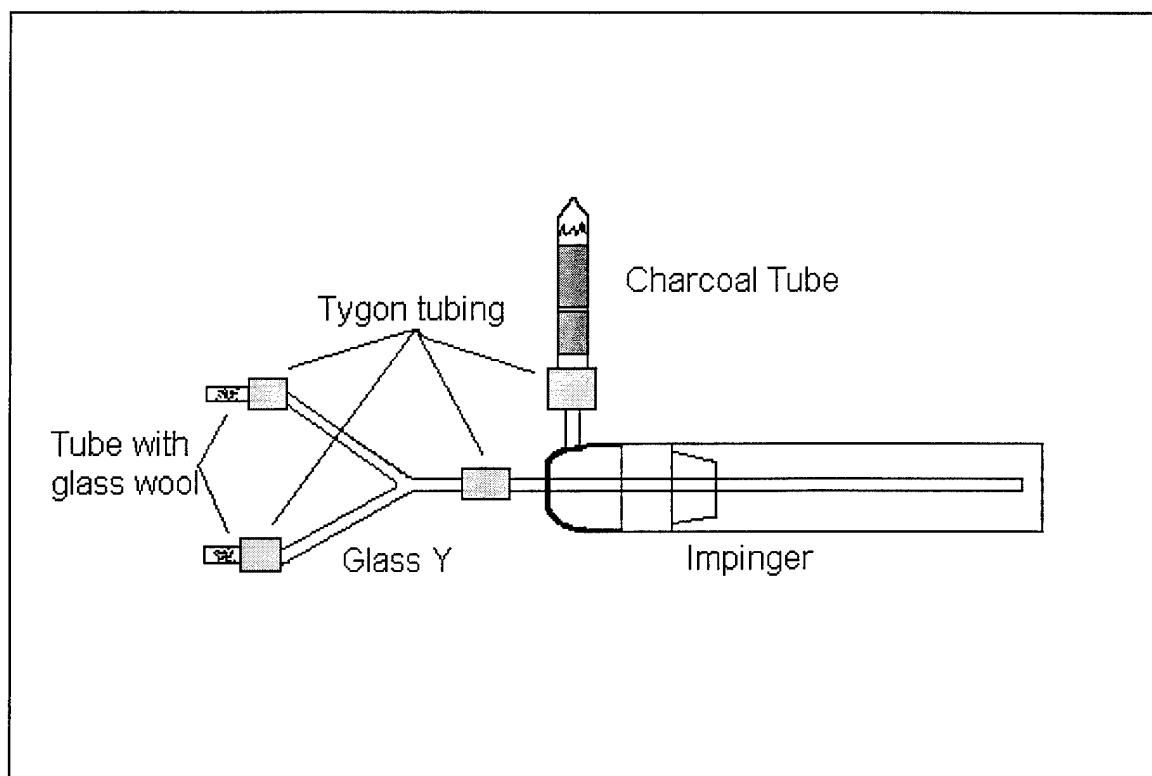


Figure 3: Vaporizing / Imparting Device

## **VIII. RESULTS**

### **Quality Control Standards and Investigations**

No breakthrough of SM was detected on the backup sections of any charcoal tubes during experiments in which SM vapor was imparted onto the activated charcoal. According to NIOSH, breakthrough should not have been significant until loads reached 40 ul. No significant amounts of SM were found adhering to the glass surfaces including glass wool plugs (trace  $<0.08$  ul/ml). Recovery efficiency in these preliminary trials was found to be  $96 \pm 4$  percent.

### **Vapor Verses Liquid Deposition/Recovery**

There were no measured differences in the recovery of styrene via liquid or vapor application to charcoal tubes over zero or twenty-four hour periods as shown in Figures 4 and 5. The liquid applied SM was slightly low in the twenty-four hour storage test, though by a slight margin. The difference was probably due to the use of a different 10 ul syringe for each test run.

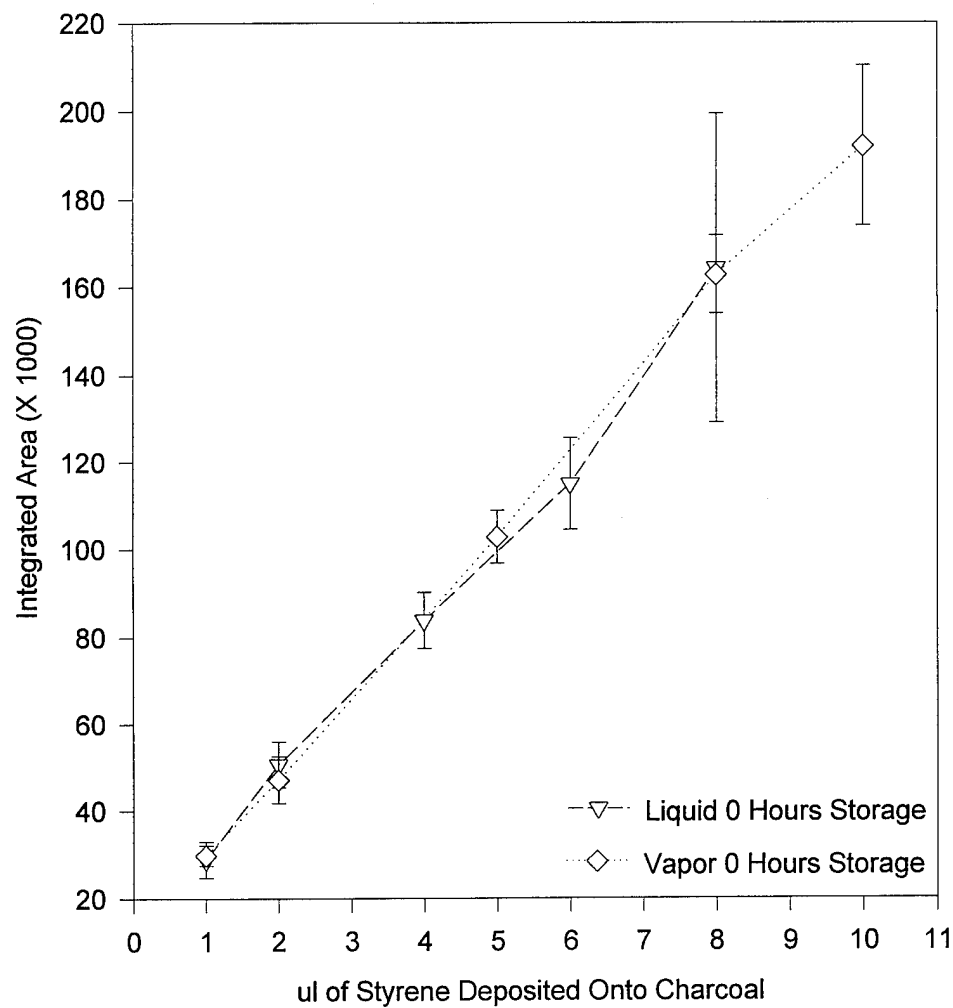


Figure 4: Comparison of SM Recovery in Liquid Verses Vapor Deposition on Charcoal After Zero Hours of Storage Time. Ninety-five percent confidence intervals are marked at each point.

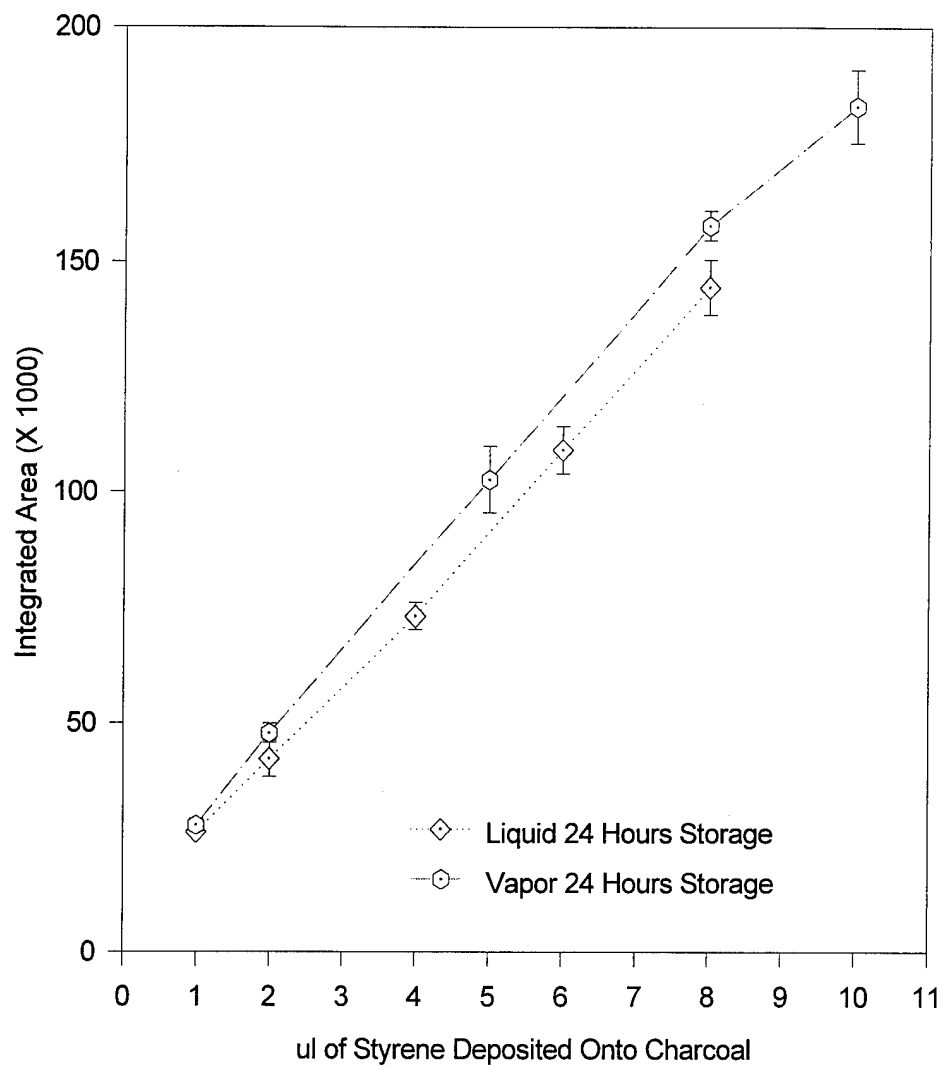


Figure 5: Comparison of SM Recovery in Liquid Verses Vapor Deposition on Charcoal After Twenty-Four Hours of Storage Time. Ninety-five percent confidence intervals are marked at each point.

## **Recovery of SM Vapors From Charcoal Tubes**

Figure 6 illustrates the recovery of specified amounts of vaporized styrene monomer stored for various periods on activated charcoal tubes. Each point on the graph represents the average recovery from three charcoal tubes with its ninety-five percent confidence interval. The linear regression line for each SM loading was then drawn. The essentially flat curves at different loadings demonstrates no effect of time on the recovery of SM on activated carbon. The slight increase in SM recovery for the 10 ul load can be explained by difficulties in accurately measuring 10 ul, using a 10 ul syringe, and potential saturation of the GC detector.



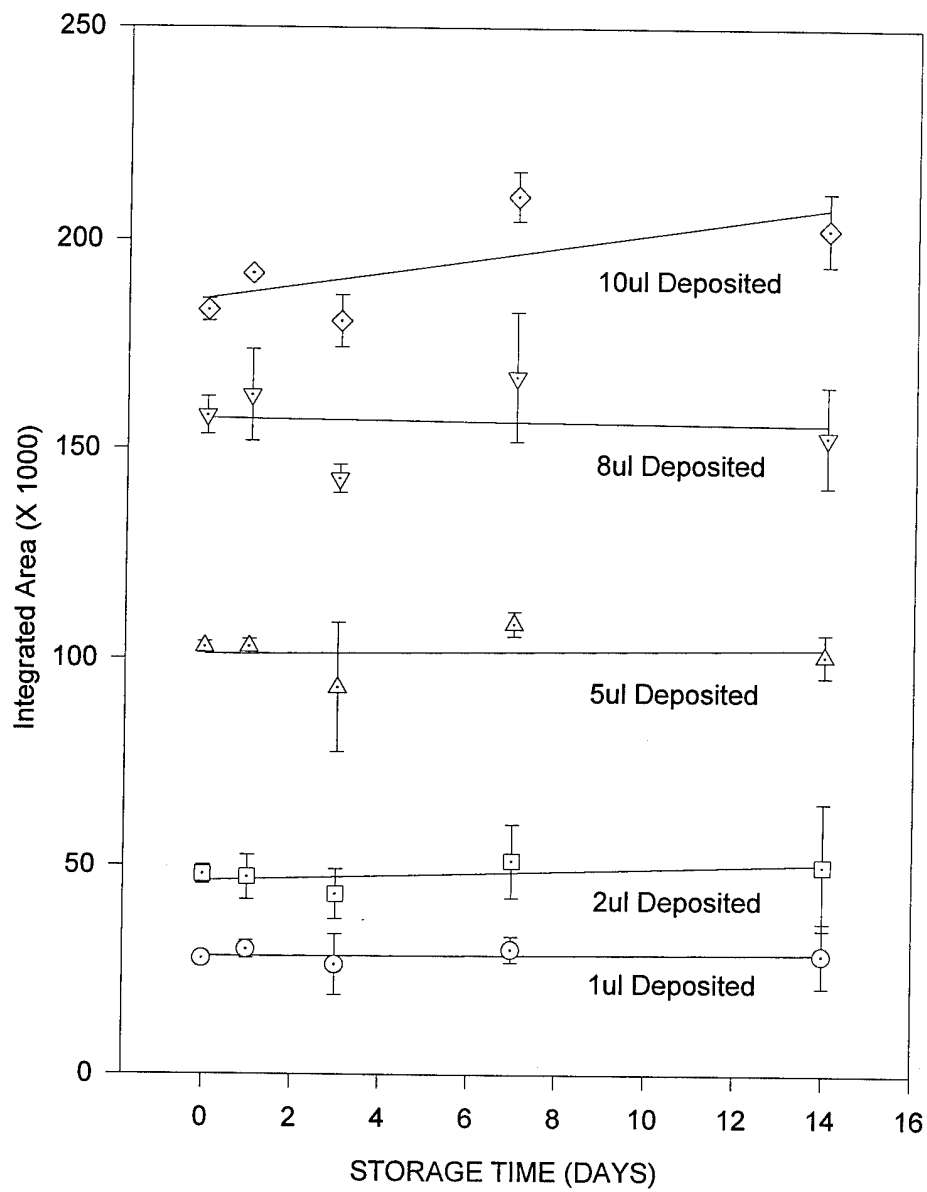


Figure 6: Recovery of Styrene Monomer Vapors From Unactivated Charcoal Over Time

### **Recovery of Activated SM From Charcoal Tubes**

Figure 7 shows the overall recovery of MEKP activated SM over time. Each bar represents the mean for six charcoal tubes. The ninety-five percent confidence interval is presented for each mean. As previously noted, SM and SM/DMP served as reference controls.

Table 3 shows the ANOVA for aforementioned data (Figure 7), examining the recovery of activated SM over time relative to that for SM alone and DMP/SM controls. The Analysis of Variance demonstrated no relationship between the amount of SM recovered and presence of other chemicals, DMP, or MEKP (F-Ratio = 0.67, probability level = 0.5123, and the power was 0.1435). The ANOVA also showed no relationship between the amount of SM recovered and storage time, as did the first investigation, (F-Ratio = 1.81, probability level = 0.1044, and the power was 0.5945). The ANOVA did show a slight relationship between storage time and chemical agent (F-Ratio = 2.88, probability level = 0.0018, and the power was 0.9738). This result was noted for the time zero storage data with SM alone in which two tubes had unusually low recovery of SM and in one tube of the 0.5 hour storage data for the SM/MEKP test which had one unusually low recovery of SM. The low recovery actually represents less accurate (low) loadings of SM liquid onto the glass wool plug.

Figure 8 represents the composite data comparing SM, SM/DMP, and SM/MEKP-DMP.

The graph removes time as a factor from the second experiment and demonstrates only the effects of the various chemical deposition protocols on the recovery of SM. All data from the seven storage periods were combined according to the chemical combination, accounting for a total of forty-two charcoal tubes per chemical combination. The average recovered SM by protocol with its ninety-five percent confidence interval is shown.

Source		Sum of	Mean		Prob	Power
<u>Term</u>	<u>DF</u>	<u>Squares</u>	<u>Square</u>	<u>F-Ratio</u>	<u>Level</u>	<u>(Alpha=0.05)</u>
Chem. Protocol	2	3.992E+7	1.996+7	0.67	0.5123	0.1436
Time Stored	6	3.217E+8	5.362E+7	1.81	0.1045	0.5945
Chem. and Time	12	1.024E+9	8.537E+7	2.88	1.811E-3	0.9739
Error	105	3.114E+9	2.965E+7			
Total (Adj)	125	4.500E+9				
Total	126					

Table 3: Analysis of Variance (ANOVA)

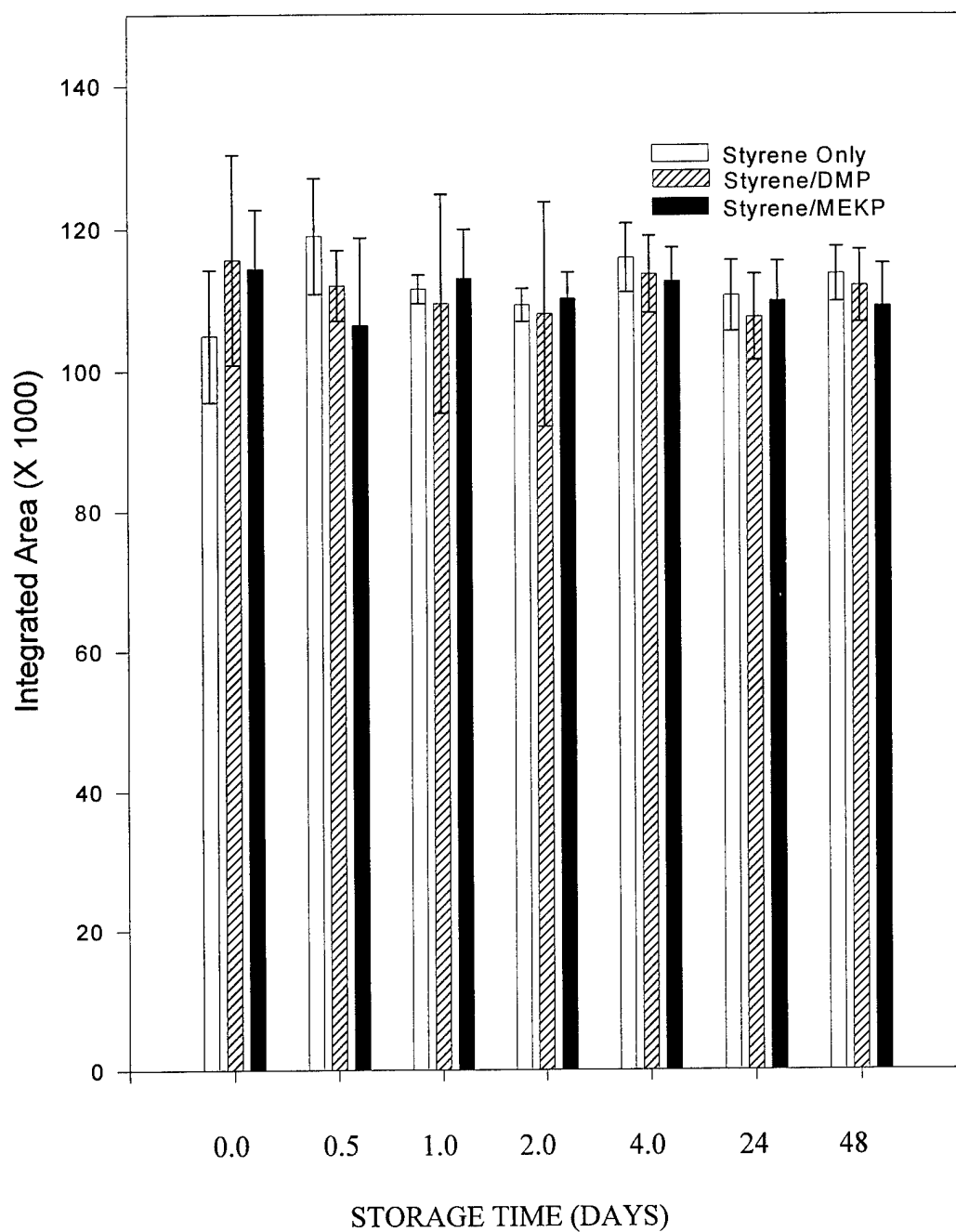


Figure 7: Recovery of MEKP Initiated Styrene Monomer Vapors From Activated Charcoal Over Time After Loading With 5 ul of Styrene Monomer

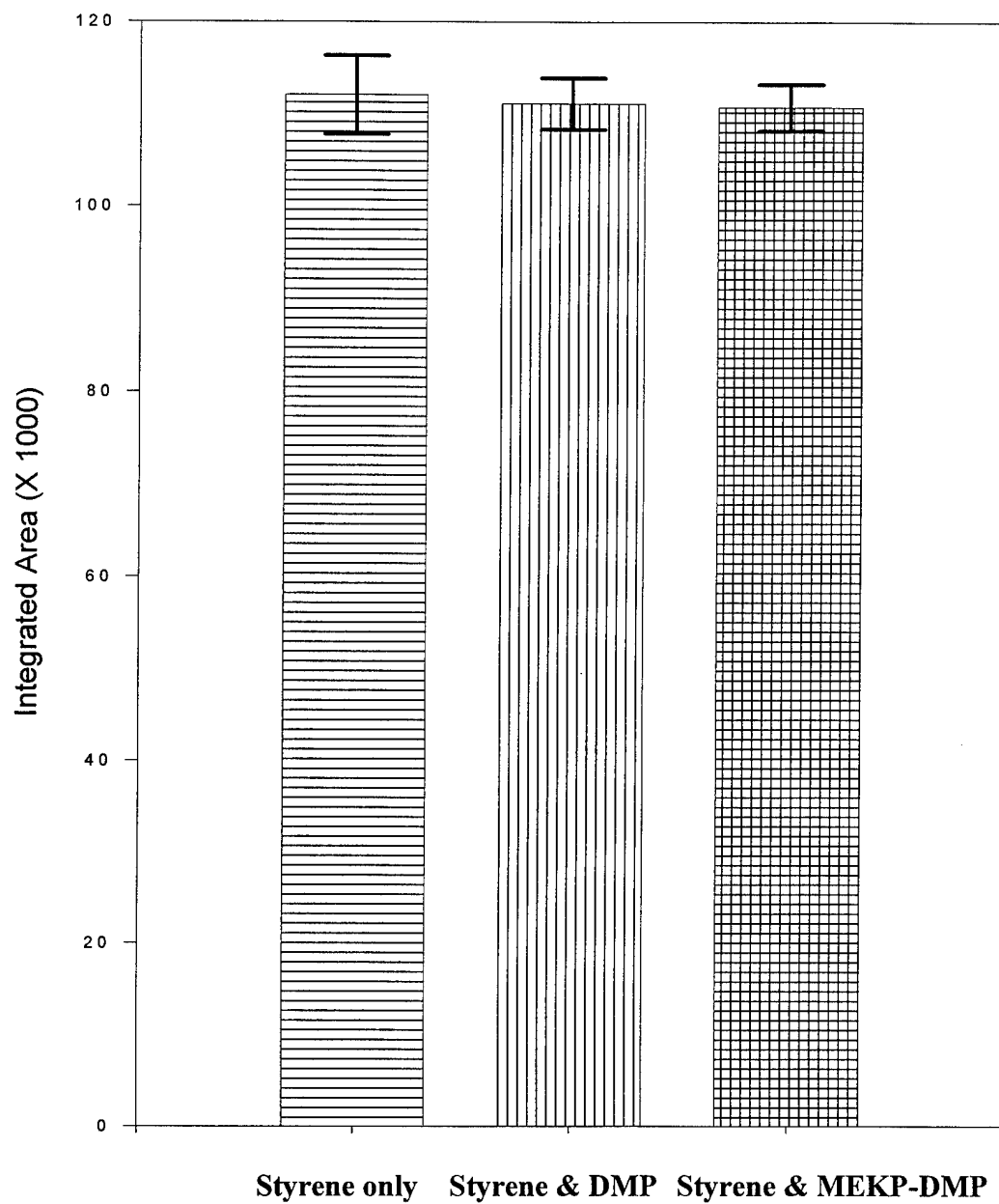


Figure 8: Comparison of Styrene Recoveries of SM for SM only Verses SM/DMP  
Verses SM/MEKP-DMP Depositions

## IX. DISCUSSION

In the evaluation of worker exposure to styrene vapors a variety of methodologies may be employed to assess the magnitude of that exposure. The monitoring of workers in industrial situation suggests that time weighted average monitoring of workers using activated charcoal tubes followed by extended storage periods may actually underestimate exposures to styrene monomer vapors due to polymerization of free SM. Styrene alone is known to be a self-polymerizer. This reaction is accelerated polymerization due to the co-presence of initiators like MEKP. The polymerization of SM makes SM unavailable for analysis.

The study conducted here indicates that SM alone does not self polymerize to any measurable extent over the time periods and charcoal loadings tested (see Figure 6). It would appear that uninitiated SM should be stable on activated charcoal tubes at room temperature for periods up to two weeks. The recovery of SM over this period was essentially 100%.

The recovery of vaporized SM mixed with the polymerizing agent, MEKP, was investigated under controlled conditions to evaluate the potential losses of SM due to the

polymerization process. Interestingly, no loss of SM was detected over the course of a two day period, despite sufficient time for polymerization to have taken place (see Figure 7). There are several possible explanations for this observation. Either insufficient contact of SM and MEKP occurred to promote polymerization of the SM while in the vapor phase, or chemical desorption with carbon disulfide somehow liberates SM from the polymer matrix. Preliminary studies at this industrial hygiene laboratory have revealed that styrene is not leached from formed polymer.

A follow-up study to examine in detail the availability of SM from MEKP polymerized styrene should be undertaken using liquid mixing (MEKP and SM) techniques. In the event that SM is not significantly recovered from polymerized styrene during desorption, a vapor generation and polymerization protocol should be developed to ensure that polymerization takes place prior to deposition on the activated charcoal.

Further field investigations to explain the discrepancies between the charcoal tube monitoring and IR analyzer or indicator tube monitoring should also be more critically investigated. Short term charcoal tube monitoring should be carefully matched with infrared monitoring at identical locations to further validate discrepancies previously noted.



## **X. CONCLUSION**

The stability and recovery of styrene monomer on activated charcoal tubes was investigated with and without the presence of an initiator, MEKP. Based on these studies, styrene monomer alone was found to be stable on activated charcoal for up to two weeks at room temperature for loadings within the recommended range of NIOSH (2.17 - 8.49 mg SM). Styrene monomer was also fully recoverable after two days following the mixing of SM vapors with the polymerizing agent, MEKP. This observation suggests the need to re-examine the mixing protocol for SM and MEKP to ensure that sufficient contact was provided to promote the polymerization process.

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